

Gas Chromatographic Separation of Long-chain Fatty Acid Methyl Esters on Polyvinyl Acetate

POLYESTER-TYPE partitioning media for the separation of mixtures of the methyl esters of long-chain saturated and unsaturated fatty acids by gas chromatography have recently been reported^{1,2,3}. Some of these materials tend to 'bleed' excessively at the temperatures required for the separation of the fatty acid esters. In addition, polyesters from the same polyglycols and dibasic acids, when prepared in different laboratories, may have dissimilar properties since the average molecular weight, as well as the distribution of molecular weight in the final polymer mixture, is not adequately controlled.

We wish to report on the use of commercially available polyvinyl acetates to separate completely the methyl esters of stearic, oleic, linoleic, and linolenic acids. These naturally occurring C₁₈ acids are those least amenable to separation.

The thermal degradation of polyvinyl acetate has been studied⁴. The products of degradation are acetic acid and polyvinylacetylene. Acetic acid reportedly becomes detectable at 210°C. In preliminary stability studies we found that for a freshly prepared column at a helium gas flow of 100 ml./min. at 195°C. the amount of acetic acid formed was less than 0.1 mgm./hr. per gram of polyvinyl acetate. At 205°C. acetic acid was evolved at the rate of 0.5 mgm./hr. per gram of polyvinyl acetate; at 230°C. this rate was 1.5 mgm./hr. of acetic acid per gm. of polyvinyl acetate. This rate of acetic acid evolution decreased with time without impairing the efficiency of the column. In all studies the base line drift was less than ± 0.2 mv. The infra-red spectra of the products collected at 230°C. over a 12-hr. period indicated the presence of acetic acid only. Thus, if the fatty acid methyl esters separated by the use of a polyvinyl acetate column are collected for further study, any trace impurities from the column can be readily removed, or easily compensated for in spectrophotometric studies.

The results reported in Table I were obtained using a polyvinyl acetate polymer of a rather low degree of polymerization with a molecular weight of approximately 1500. Similar results were obtained with a polyvinyl acetate polymer of molecular weight of approximately 23,000.

TABLE 1

Compound	Retention vol. (ml.)*
Methyl palmitate	1080
Methyl stearate	1860
Methyl oleate	2100
Methyl linoleate	2350
Methyl linolenate	2750
Methyl arachidonate	5230

* Retention volumes calculated for a flow-rate of 83 ml./min. and measured from the time of emergence of the solvent phase.

An 8-ft. coiled copper column, $\frac{1}{4}$ in. outside diameter and wall thickness 0.03 in., was used. The partition medium consisted of 15 per cent polyvinyl acetate, designated as 'Vinylite AYAC'⁵, of a molecular weight of approximately 1500 on 'Chromosorb', 30-60 mesh⁶. The column packing was prepared by slurring the 'Chromosorb' with a 10 per cent solution of the polymer dissolved in acetone. The acetone was evaporated at room temperature and stray volatile materials removed by heating in a vacuum oven at 130°C. The gas chromatograph was a commercial model⁷ provided with a 1-mv., 1-sec. full-scale strip-chart recorder⁸. The detector was a 4-filament thermal conductivity unit. The helium flow rate was 83 ml./min. measured at the column exit and at room temperature. The column and cell temperature was 205°C. The pressure drop across the column was 30 p.s.i.g. Two mgm. of each methyl ester were dissolved in petroleum ether (b.p. 37°) and a 5- μ l. sample injected into the column. Values for methyl palmitate and methyl arachidonate are included in Table 1 for comparative purposes.

Quantitative estimation of the fatty acid esters within ± 5 per cent could be made by measuring the peak areas and comparing these values with those obtained from known amounts of the pure methyl esters.

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¹ Orr, C. H., and Callen, J. E., *J. Amer. Chem. Soc.*, **80**, 249 (1958).

² Lipsky, S. R., Landowne, R. A., and Godet, M. R., *Biochim. Biophys. Acta*, **31**, 336 (1959).

³ Craig, B. M., and Murty, N. L., *Can. J. Chem.*, **36**, 1297 (1958).

⁴ Grassie, N., *Trans. Faraday Soc.*, **48**, 380 (1952).

⁵ Union Carbide and Carbon Corp., Bakelite Division, New York, New York.

⁶ Johns-Mansville, Celite Division, New York, New York.

⁷ A Beckman GC-2 gas chromatograph was used.

⁸ The recorder was manufactured by Minneapolis-Honeywell, Brown Instrument Division, Philadelphia, Pennsylvania.